PTO 07-5249

CC = JP
19920204
Kokai
04032577

COATED AL OR AL ALLOY MATERIAL WITH EXCELLENT COATING FILM ADHERANCE AND CORROSION RESISTANCE

[Tomaku mitsuchakusei oyobi taishokusei ni sugureta tosho Al matawa Al gokinzai]

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UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. JULY 2007
TRANSLATED BY: THE MCELROY TRANSLATION COMPANY

PUBLICATION COUNTRY	(19):	JP
DOCUMENT NUMBER	(11):	04032577
DOCUMENT KIND	(12):	Kokai
PUBLICATION DATE	(43):	19920204
APPLICATION NUMBER	(21):	02136639
APPLICATION DATE	(22):	19900525
INTERNATIONAL CLASSIFICATION[5]	(51):	C 23 C 22/24, B 05 D 7/14, B 32 B 15/08, C 23 C 22/07, C 25 D 11/16, 11/36, 11/38
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APPLICANT	(71):	Kobe Steel, Ltd.
TITLE	(54):	COATED AL OR AL ALLOY MATERIAL WITH EXCELLENT COATING FILM ADHERANCE AND CORROSION RESISTANCE
FOREIGN TITLE	[54A]:	Tomaku mitsuchakusei oyobi taishokusei ni sugureta tosho Al matawa Al gokinzai

Claims

1. A type of coated Al or Al alloy material with excellent coating film adherance and corrosion resistance characterized by the fact that a film containing 20-60 wt% and which is formed as porous structure or rough surface structure by means of plural pores with true surface area (S_o) three or more times the apparent surface area (S_a) when the surface look is smooth is formed on the surface of the Al or Al alloy material, and at the same time, a resin coating film is formed on said film, and said film and said coating film are bonded to each other by means of hydrogen bonds.

2. The coated Al or Al alloy material described in Claim 1, characterized by the fact that the film is mainly made of a phosphate compound or chromate compound.

3. The coated Al or Al alloy material described in Claim 1, characterized by the fact that the film is mainly made of a metal oxide or metal hydroxide.

4. A type of coated Al or Al alloy material, characterized by the fact that the film is a porous alumite film with porosity of 60-98% and with film thickness of 0.5 μm or thicker.

Detailed explanation of the invention

Industrial application field

The present invention pertains to a type of coated Al or Al alloy material with excellent coating film adherance and corrosion resistance after coating. Such coated Al or Al alloy material can be used as the outer sheet material of various home appliances and building materials.

Prior art

Al or Al alloy material (hereinafter to be referred to as Al alloy material) has lighter weight than iron/steel material and is more beautiful, and it has excellent corrosion resistance. Consequently, it has

been adopted in various applications. Recently, however, in order to improve the quality, the requirement of corrosion resistance of the Al alloy material has become even higher. As a result, the conventional Al alloy material with only inactive film formed on it is unable to meet the demand of the customers. Also, for the Al alloy material, colors and patterns are attached to improve the appearance. However, as the surface of the Al alloy material has a fine inactive oxide film (inactive film), as the paint is directly coated, good coating film adherance cannot be realized. As a result, in the prior art, before the coating operation, chromate processing, alumite processing or the like is performed to improve the adherance (pretreatment of coating).

Problems to be solved by the invention

However, the effects in improving the coating film adherance and corrosion resistance after coating realized by the aforementioned pretreatment of coating in the prior art are insufficient to meet the ever increasing demands of the customers. Consequently, there is a demand for development of a type of coated Al alloy material that can display excellent coating film adherance and corrosion resistance after coating even under a severe application environment. The purpose of the present invention is to solve the aforementioned problems of the prior art by providing a type of coated Al alloy material characterized by the fact that by forming a layer for improving the corrosion resistance and coating film adherance between the Al alloy base material and the coating film, it is possible to further improve the coating film adherance and corrosion resistance after coating of the coated Al alloy material.

Means to solve the problems

In order to realize the aforementioned purpose, the present invention provides a type of coated Al or Al alloy material with excellent coating film adherance and corrosion resistance characterized by the

fact that a film formed as a porous structure or rough surface structure by means of plural pores with true surface area (S_o) three or more times the apparent surface area (S_a) when the surface look is smooth is formed on the surface of the Al or Al alloy material, and, at the same time, a resin coating film is formed on said film, and said film and said coating film are bonded to each other by means of hydrogen bonds.

Operation

It is believed that in order to improve the coating film adherance for the Al alloy material, it is necessary to find the causes dominating the adherance between the feed material as the workpiece and the coating film, and the present inventors have performed various studies. As a result, it has been found that (1) the surface shape of the feed material and (2) the hydrogen bonding force between the feed material and the coating film are major factors determining the coating film adherance. That is, when the surface of the feed material is formed as a porous surface and/or rough surface, the effective bonding area with the coating film is increased, and at the same time, the coating film adherance is increased by the anchoring effect. Also, when there exists a film made of oxide, hydroxide or other oxygen-containing compound on the surface of the feed material, hydrogen bonds are formed between the hydroxyl groups and amino groups, and other polar groups in the molecules that form the coating film and said oxygen-containing film. Due to a synergic effect of said effects, the coating film adherance can be improved significantly.

Here, studies have been performed on the influence on the coating film adherance when the Al alloy material is processed using mechanical or chemical means to form a rough surface or porous structure, and when the Al alloy material is processed by means of oxidation treatment, chemical treatment, etc., so as to form an oxygen-containing film with a rough surface or porous surface. The results indicate that

when the true surface area (S_o) of the rough or porous film surface is three or more times the apparent surface area (S_a) when it looks smooth, the anchoring effect can be well displayed. Also, when the oxygen content in the film surface is in the range of 20-60%, the effect of the hydrogen bonds in improving the coating film adherance can be displayed efficiently. By means of a combination of said effects, it is possible to significantly improve the coating film adherance, and at the same time, it is possible to improve the corrosion resistance after coating, too.

In other words, as the true surface area (S_o) of said oxygen-containing film is less than three times the apparent surface area (S_a), a sufficient anchoring effect with the coating film cannot be displayed, and the coating film adherance and corrosion resistance after coating also are insufficient. Also, when the oxygen content on the film surface is less than 20%, a sufficient hydrogen bonding force cannot be realized with the coating film, and the satisfactory effect in improving the coating film adherance also cannot be realized. On the other hand, if the oxygen content is over 60%, the film itself becomes brittle and weak, and the oxygen-containing film can easily be separated from the Al alloy base material. As a result, the characteristic features of the present invention cannot be displayed in this case.

According to the present invention, the true surface area (S_o) and the oxygen content on the surface of the Al alloy material are defined as mentioned previously. There is no specific restriction on the method for forming the oxygen-containing film that can meet the aforementioned requirements. The following methods, however, are preferred.

(1) A method of formation of the oxygen-containing film on the surface after the surface of the Al alloy material is subjected to roughening treatment.

(2) A method of formation of a porous oxygen-containing film on the surface of the Al alloy material.

The surface roughening treatment methods adopted for embodiment of said method (1) include shot blast and other mechanical methods, etching and other chemical methods, etc. Methods for forming said oxygen-containing film include oxidation method by heating in the atmosphere, chromate processing method, etc. The methods for forming the porous oxygen-containing film in said method (2) include phosphate salt processing method and other chemical treatment methods, alumite processing method, flame spraying method of porous oxide, etc.

The thickness of the oxygen-containing film formed in this way should be 0.1 μm or thicker, or preferably 0.2 μm or thicker. With such thickness, it is possible to sufficiently improve the coating film adherance.

Especially, porous alumite film is a preferable oxygen-containing film. In particular, the porous alumite film with porosity in the range of 60-98% and with film thickness of 0.5 μm or thicker has excellent anchoring effect and hydrogen bonding force, and it can provide a coated Al alloy sheet with excellent coating film adherance and corrosion resistance after coating.

There is no specific restriction on the type of the paint for coating on the surface of the oxygen-containing film. For example, one may use a paint mainly made of a resin having hydroxyl groups, amino groups or other polar groups in its molecules. Examples of the preferable types include epoxy resin, alkyd-melamine resin, acrylic resin, polybutadiene resin, etc. Especially, the epoxy resin and alkyd-melamine resin are preferred.

There is no specific restriction on the shape of the Al alloy material in the present invention. In addition to the sheet material that is used most widely, one may also use wires, rods, tubes, etc.

Application examples

Application Example 1

For Al alloy sheets (5082), various treatments for forming an oxygen-containing film as listed in Table 1 were performed to form films with different ratios of true surface area (S_o)/apparent surface area (S_a) and different oxygen contents, respectively. Then, an alkyd-melamine resin of the baking curing type was coated on the surface of each film sample with an appropriate amount corresponding to a dry film thickness of about 20 μm, followed by baking treatment at 130°C for 20 min, forming coated Al alloy sheets. Here, the true surface area (S_o) was measured using an electrochemical method (measurement of the current when a constant potential is applied), and the oxygen content of the film surface and thickness of the film were measured using AES analysis method.

For each obtained coated Al alloy sheet sample, the coating film adherance and corrosion resistance after coating were measured using the following listed methods, with results listed in Table 1.

Coating film adherance

The sheet sample is dipped in ion-exchanged water at 50°C for 240 h, followed by checkerboard tape peeling test. In this case, the number of the peeled sites of the coating film is determined, and evaluation is performed with the following grades.

O: Peeling site number less than 1/100: Good

Δ: Peeling site number in the range of 2-5/100: OK

X: Peeling site number more than 8/100: Poor

Corrosion resistance after coating

A cross cut is formed on the sample sheet, and four cycles are performed in the treatment repeatedly with each cycle composed of the following procedure: [spray with saline for 24 h] → [wetting test: 80% RH x 50°C x 12 h] → [setting at room temperature for 24 h]. Then, based on the largest length of rust string generated, evaluation is performed with the following grades:

O: maximum rust string length <1 mm

Δ: maximum rust string length in the range of 1-4 mm

X: maximum rust string length >4 mm

TABLE 1

No.	処理方法	$(S_a)/(S_o)$	酸素含有皮膜表面の酸素量（重量%）	酸素含有皮膜の厚さ（μm）	塗膜密着性	塗装後耐食性	
1	ショットブラスト＋クロメート処理	3.2	35	0.1	○	○	本発明例
2	エッチング＋大気酸化処理	3.6	43	0.2	○	○	
3	エッチング＋アルマイト処理	5.6	48	10	○	○	
4	アルマイト処理	4.8	55	2	○	○	
5	燐酸亜鉛処理	6.3	32	5	○	○	
6	燐酸亜鉛＋クロメート処理	6.2	28	5	○	○	
7	Al_2O_3 溶射	4.2	45	3	○	○	
8	Al溶射＋クロメート処理	3.5	25	0.2	○	○	
9	−	1.2	18	0.01	×	×	比較例
10	エッチング	1.6	18	0.03	×	×	
11	アルマイト処理	2.8	38	0.2	△	×	
12	クロメート処理	1.8	40	0.05	○	△	
13	Al溶射＋大気酸化処理	3.8	52	5	×	×	
14	エッチング＋大気酸化処理	3.3	45	0.09	△	×	参考例

Key: 1 Processing method

2 Oxygen content in the surface of the oxygen-containing film (wt%)

3 Thickness of oxygen-containing film (μm)

4 Coating film adherance

5 Corrosion resistance after coating

6 Shot blast + chromate treatment

Etching + atmosphere oxidation treatment

Etching + alumite treatment

Alumite treatment

Zinc phosphate treatment

Zinc phosphate + chromate treatment

Al_2O_3 flame spraying

Al flame spraying + chromate treatment

7 -

Etching

Alumite treatment

Chromate treatment

Al flame spray + atmosphere oxidation treatment

8 Etching + atmosphere oxidation treatment

9 This invention

10 Comparative Example

11 Reference Example

As can be seen from Table 1, in Experiment Nos. 1-8 that meet the constitutional requirements of the present invention, both the coating film adherance and corrosion resistance after coating are excellent.

On the other hand, in Experiment Nos. 9-13 that do not meet the constitutional requirements of the present invention, the results are undesired. More specifically, in Experiment No. 9, neither surface

roughening treatment nor oxygen-containing film formation treatment are performed. In Experiment No. 10, only surface roughening treatment is performed, while oxygen-containing film formation treatment is not performed. In Experiment Nos. 11 and 12, only the oxygen-containing film formation treatment is performed, while the surface roughening treatment is not performed. Consequently, the coating film adherance and/or corrosion resistance after coating are poor. In addition, in Experiment No. 13, after surface roughening treatment, oxidation treatment is performed, yet the oxygen concentration of the surface of the oxide film is over the defined range. As a result, the film is brittle and weak, and adherance between the Al alloy material and the oxide film is poor, so that peeling takes place from this portion. Consequently, both the coating film adherance and corrosion resistance after coating are poor.

In the reference example as Experiment No. 14, surface roughening treatment and oxygen-containing film formation treatment are performed, yet the oxygen-containing film is too thin, so that both the coating film adherance and the corrosion resistance after coating are little improved. Said experimental data indicate that the film thickness of the oxygen-containing film should be 0.1 μm or thicker.

<u>Application Example 2</u>

On the surface of a cleaned Al alloy sheet (5032), constant-current anodizing was performed in a solution of phosphoric acid, sulfuric acid, chromic acid or oxalic acid to form a porous alumite film. Then, alkyd-melamine resin or epoxy resin was directly coated on the film, forming the coated Al alloy sheet with constitution listed in Table 2.

(Coating film adherance): Same as mentioned previously

(Corrosion resistance after coating)

For each sample sheet, after a cross cut is performed on each of the Al alloy base materials, brine spraying is performed for 840 h, and the width of swelling of the coating film from the cross-cut portion (half the two-side maximum value) is used to make an evaluation with the following grades.

O: Swelling width <0.5 mm

Δ: Swelling width in the range of 0.5-3 mm

X: Swelling width >3 mm

TABLE 2

		アルマイト皮膜				塗料の種類	塗膜密着性	塗装後耐食性
		膜厚 (μm)	空孔率 (%)	S_0/S_1	表面の酸素量 (%)			
本発明	25	0.5	60	8.5	51.8	アルキドメラミン系	○	○
	26	1.5	65	4.7	52.8	〃	○	○
	27	2.0	60	6.3	53.8	エポキシ系	○	○
	28	5.0	70	6.8	54.2	〃	○	○
	29	0.8	70	5.8	50.5	アルキドメラミン系	○	○
	30	1.0	60	3.2	50.3	〃	△	△
	31	0.3	70	3.4	50.5	エポキシ系	△	△
参考例	32	0.3	50	2.2	38.1	エポキシ系	×	×
	33	1.0	65	1.8	52.3	〃	×	×
	34	5.2	58	1.2	52.0	アルキドメラミン系	×	×

Key:

1 Alumite film

2 Film thickness (μm)

3 Porosity (%)

4 Oxygen content in the surface (%)

5 Type of paint

6 Coating film adherance

7 Corrosion resistance after coating

8 This invention

9 Reference Example

10	Alkyd-melamine resin
	"
	Epoxy resin
	"
	Alkyd-melamine resin
	"
	Epoxy resin
11	Epoxy resin
	"
	Alkyd-melamine resin

Figure 1 shows the results of studies of the coating film adherance (coating film peeling rate after test of coating film adherance) for the various samples with different porosity values for the oxygen-containing film made of alumite film with a thickness of about 1.0 μm. Figure 2 shows the results of the studies on the relationship between the film thickness and the coating film's swelling width in the cross-cut saline spray test for samples with alumite film having a porosity of about 70%.

As can be seen from said Table 2 and Figures 1, 2, when porous alumite is used as the oxygen-containing film, the porosity of the alumite film is set in the range of 60-98%, and the film thickness is set at 0.5 μm or thicker. It can be seen that excellent coating film adherance and corrosion resistance after coating can be guaranteed under said conditions.

Effect of the invention

According to the invention with said constitution, by including an oxygen-containing film with prescribed ratio of S_o/S_a and a prescribed oxygen content between Al or Al alloy base material and the coating film, and displaying the anchoring effect and hydrogen bonding effect with the coating film, it is possible to significantly improve the coating film adherance, and it is possible to provide a type of coated Al alloy material with excellent corrosion resistance after coating.

<u>Brief description of the figures</u>

Figures 1 and 2 are graphs illustrating the relationship between the porosity of the alumite film and the coating film peeling rate and the relationship between the film thickness of the alumite film and the coating film's swelling width.

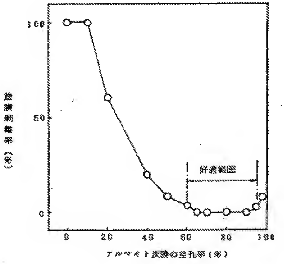

Figure 1

Key: 1 Coating film's peeling rate (%)

2 Porosity of alumite film (%)

3 Preferable range

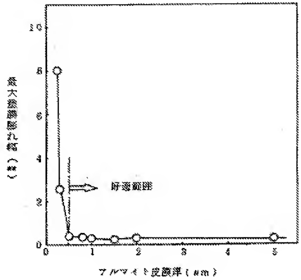

Figure 2

Key: 1 Maximum coating film's swelling width (mm)

2 Alumite film thickness (μm)

3 Preferable range